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ASSESSMENT REPORT ON

AMMONIA

**FOR DEVELOPING
AMBIENT AIR QUALITY
OBJECTIVES**

- *VOLUME II – Vegetation Effects*





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**ASSESSMENT REPORT ON
AMMONIA
FOR DEVELOPING AMBIENT AIR QUALITY OBJECTIVES
VOLUME II – VEGETATION EFFECTS**

**Prepared for
Alberta Environment**

**by
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FOREWORD

Alberta Environment maintains Ambient Air Quality Objectives to support air quality management in Alberta. Alberta Environment currently has ambient objectives for thirty-one substances and five related parameters. These objectives are periodically updated and new objectives are developed as required. Fact Sheets on Ambient Air Quality Guidelines were updated in September 1997 and February 2000.

With the assistance of the Clean Air Strategic Alliance, a multi-stakeholder workshop was held in October 2000 to set Alberta's priorities for the next three years. Based on those recommendations, a three-year work plan ending March 31, 2004 was developed to review four existing guidelines, create three new guidelines for three families of substances, and adopt six new guidelines from other jurisdictions.

This document is one in a series of documents that presents the scientific assessment for these substances.

Ahmed Idriss, Ph.D., P.Eng.
Project Manager
Science and Standards Branch

NOTE: The *Environmental Protection and Enhancement Act*, Part 1, Section 14(1) refers to "ambient environmental quality objectives" and uses the term "guidelines" in Section 14(4) to refer to "procedures, practices and methods for monitoring, analysis and predictive assessment." For consistency with the Act, the historical term "ambient air quality guidelines" is being replaced by the term "ambient air quality objectives." This document was prepared as the change in usage was taking place. Consequently any occurrences of "air quality guideline" in an Alberta context should be read as "air quality objective."

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Note to the reader: The first two sections in this supplemental report provide only a brief overview, as a preamble to the descriptions of the effects of NH_3 on terrestrial vegetation. For additional information on the topics described in these two sections, the reader is referred to the relevant portions of Volume I of the report, submitted by WBK & Associates Inc. entitled "Assessment Report on Ammonia for Developing Ambient Air Quality Objectives".

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SUMMARY

At the global scale, among all N (nitrogen) species in the atmosphere and their deposition on to terrestrial vegetation and other receptors, NH_3 (ammonia) is considered to be the foremost. The major sources for atmospheric NH_3 are agricultural activities and animal feedlot operations, followed by biomass burning (including forest fires) and to a lesser extent fossil fuel combustion. Close to its sources, acute exposures to NH_3 can result in visible foliar injury on vegetation. NH_3 is deposited rapidly within the first 4-5 km from its sources. However, NH_3 is also converted in the atmosphere to fine particle NH_4^+ (ammonium) aerosols that are a regional scale problem.

Much of our current knowledge of the effects of NH_3 on higher plants is predominantly derived from the studies conducted in The Netherlands, although there are many published reports from other parts of Europe. Adverse effects on vegetation occur when the rate of foliar uptake of NH_3 is greater than the rate and capacity for in vivo detoxification by the plants. Most to least sensitive plant species to NH_3 are native vegetation > forests > agricultural crops. There are also a number of studies on N deposition and lichens, mosses and green algae. Direct cause and effect relationships in those cases are confounded by other environmental factors, particularly changes in the ambient SO_2 (sulphur dioxide) concentrations.

In addition to the direct foliar injury, adverse effects of NH_3 on higher plants include alterations in: growth and productivity, tissue content of nutrients and toxic elements, drought and frost tolerance, responses to insect pests and disease causing microorganisms (pathogens), development of beneficial root symbiotic or mycorrhizal associations and inter species competition or bio-diversity. In all these cases, the joint effects of NH_3 with other air pollutants such as the all-pervasive O_3 or the increasing CO_2 concentrations are poorly understood.

While NH_3 uptake in higher plants occurs through the shoots, NH_4^+ uptake occurs through the shoots, roots and through both pathways. However, NH_4^+ is immobile in the soil and is converted to NO_3^- (nitrate). In agricultural systems, additions of NO_3^- to the soil (initially as NH_3 or NH_4^+) and the consequent increases in the emissions of N_2O (nitrous oxide, a greenhouse gas) and leaching of NO_3^- into the ground and surface waters are of major environmental concern.

At the ecosystem level NH_3 deposition cannot be viewed alone, but in the context of total N deposition. There are a number of forest ecosystems in North America (including Canada) that have been subjected to N saturation and the consequent negative effects. Regulatory mitigative approaches to these problems include the use of N saturation data or the concept of critical loads. Current information suggests that a critical load of 5-10 kg ha⁻¹ yr⁻¹ of total N deposition (both dry and wet deposition combined of all atmospheric N species) would protect the most vulnerable terrestrial ecosystems (heaths, bogs, cryptogams) and values of 10-20 kg ha⁻¹ yr⁻¹ would protect forests, depending on their soil conditions. However, to derive the best analysis, the critical load concept should be coupled to the results and consequences of N saturation.

1.0 INTRODUCTION

Naturally occurring nitrogen (N_2) constitutes 78% of the dry troposphere (up to 10-15 km above the earth's surface). However, additions of anthropogenic (human-made) nitrogen (N) compounds constitute one of the four major classes of air pollutants of significance to human health and the environment. The other three classes are sulphur compounds, volatile and semi-volatile organic compounds and toxic metals (Finlayson-Pitts and Pitts, 1999). Atmospheric N species occur as gases, vapours (hydrated gas molecules) and particles (both solid and liquid). These are oxides of nitrogen (NO_x , composed of nitric oxide, NO and nitrogen dioxide, NO_2), ammonia (NH_3) and nitrous oxide (N_2O), peroxy acyl nitrates (peroxy acetyl nitrate or PAN being the most studied among them), nitric acid (HNO_3), ammonium (NH_4^+) and other inorganic and organic nitrates (NO_3^- s).

Among the atmospheric N species, NH_3 is emitted by a large number of sources such as volatilization from animal waste and synthetic fertilizers, biomass burning (including forest fires), losses from soils under native vegetation and agricultural crops, emissions from human excreta and fossil fuel combustion (Olivier et al., 1996; Lee et al., 1997; Bouwman et al., 1997).

Total anthropogenic emissions of NH_3 , NO_x and N_2O respectively account for 43.0 (36%), 31.1 (26%) and 3.2 (approx. 3%) million tons of N annually to the total global budget that includes natural sources (Olivier et al., 1998). Of the total anthropogenic emissions, NH_3 accounts for 55%, NO_x for 40% and N_2O for about 5%. With regard to total N (all three species combined) emissions, agriculture is by far the largest source (about 50%) and stationary and mobile source fossil fuel combustion each contributes 15%, whereas biomass burning contributes another 10%.

It was estimated that during 1990, China emitted 8,449 Gg NH_3 -N yr^{-1} (1 Gg = 10^9 g). In contrast estimates for USA and Canada were respectively 2,898 and 456 Gg (Olivier et al., 1998).

2.0 ATMOSPHERIC CHEMISTRY, TRANSPORT, CONCENTRATIONS AND DEPOSITION OF AMMONIA (NH₃) AND AMMONIUM (NH₄⁺) ON TO VEGETATION AND SOILS

2.1 Chemistry

NH₃ is a very important basic compound in the atmosphere. It reacts readily with acidic substances such as sulfuric acid (H₂SO₄), nitric acid (HNO₃), nitrous acid (HNO₂), or hydrochloric acid (HCl) to form ammonium salts that occur predominantly in the fine particle (size < 2.5 µm) fraction (Finlayson-Pitts and Pitts, 1999). A small amount of NH₃ (approximately 1%) reacts with hydroxy (OH) radicals to form NH₂ + H₂O, which is subsequently oxidized to NO by HNO₃ (Galbally and Roy, 1983).

The formation of fine particulate NH₄⁺ salts is a very effective mechanism in removing gaseous NH₃ from the atmosphere. Estimates of the conversion rates of NH₃ to NH₄⁺ vary between 10⁻³ s⁻¹ (Vermetten et al., 1985) and 5 X 10⁻⁵ s⁻¹ (Erisman et al., 1988). This conversion is most effective in the lowest (100 m) layer of the atmosphere above the surface (Lenhard and Gravenhorst, 1980) and is much faster during the daytime than at night (Erisman et al., 1988).

2.2 Transport

Since NH₃ is either readily converted to NH₄⁺ or subjected to dry deposition, high concentrations are found only close to the surface and near to emission sources. With discrete or isolated NH₃ sources, concentrations decrease significantly within the lower 200 m of the atmosphere (Vermetten et al., 1985; Erisman et al., 1987) and can reach background levels at 1500 m in the winter and 3000 m in the summer (Georgii and Müller, 1974; Georgii and Lenhard, 1978; Lenhard and Gravenhorst, 1980; Levine et al., 1980; Alkezweeny et al., 1986). Horizontal concentration profiles show a clear decrease with increasing distance from the source (50% reduction at 600 m from the source (Erisman et al., 1987) and 70% decrease at 4 km (Asman et al., 1989). Different estimates have been reported for the residence time of NH₃ ranging from 2.8 h during the daytime and 5 h at night (Erisman et al., 1988), 0.8 days (Möller and Schieferdecker, 1985), 1-4 days (Söderlund and Svensson, 1976) and 4 days (Dawson, 1984).

In the atmosphere, laws of gravity do not readily influence fine particle deposition on to surfaces. They are transferred on to surfaces by Brownian motion and thus ammonium sulfate [(NH₄)₂SO₄] and ammonium nitrate [NH₄NO₃] have low deposition velocities and prolonged atmospheric residence times. Assuming an atmospheric residence time of 6 days and a wind velocity of 5 m s⁻¹, the transport distance of (NH₄)₂SO₄ and NH₄NO₃ may be as large as 2,500 km (Irwin and Williams, 1988).

Vertical profiles of NH₄⁺ concentrations are far less pronounced than NH₃. In contrast to NH₃ (high concentrations close to the surface), NH₄⁺ concentrations were found to be higher than NH₃ at heights above 200 m (Georgii and Lenhard, 1978; Lenhard and Gravenhorst, 1980; Vermetten et al., 1985; Erisman et al., 1987, 1988). Horizontal profiles of NH₄⁺ were also rather homogeneous (Allen et al., 1988; Janssen et al., 1989) with only relatively small increases near NH₃ sources (Vermetten et al., 1985). Estimates of the residence time of NH₄⁺ were 4-7 days

(Bonis et al., 1980), 7.7 days (Möller and Schieferdecker, 1985), 7-19 days (Söderlund and Svensson, 1976) and 15 ± 9 days (Böttger et al., 1978).

2.3 Concentrations

Atmospheric NH_3 concentrations are not routinely measured by governmental air quality monitoring networks. This has led to significant uncertainties in the calculations of total dry deposition of N (Krupa and Moncrief, 2002). Only recently, easy to use reliable passive sampling methods for NH_3 have been developed (Krupa and Legge, 1999a). In contrast, in the context of the occurrence of acidic precipitation, NH_4^+ concentrations in wet deposition have been measured by a number of major monitoring networks, both in Canada (Canadian Network for Sampling Acid Precipitation, CANSAP or Canadian Air and Precipitation Monitoring Network, CAPMoN) and in the US (National Atmospheric Deposition Program, NADP or the National Trends Network, NTN), as well as in other parts of the world (Krupa, 2002). However, improper sampling of precipitation can lead to significant underestimations of its NH_4^+ concentrations (Krupa, 2002).

In remote areas, NH_3 concentrations can be quite low, < 50 ppt ($0.035 \mu\text{g m}^{-3}$) (Lewin et al., 1986; Alkezweeny et al., 1986), whereas close to sources such as agricultural areas and cattle feedlot operations, they can be about three orders of magnitude larger. In Alberta, Legge et al. (1990a) in a two-year study found a mean background NH_3 concentration of $0.26 \mu\text{g m}^{-3}$ (0.37 ppb or 370 ppt). In contrast, in an agricultural area, the corresponding concentrations were 1.5 to $2.0 \mu\text{g m}^{-3}$ (2.16-2.88 ppb), with the maxima ranging from 8.3 to $11.9 \mu\text{g m}^{-3}$ (11.95-17.14 ppb) (Legge et al. 1990b). As a comparison, at Claremont, California, NH_3 concentrations ranged from 57 ppb ($39.67 \mu\text{g m}^{-3}$) when the winds were blowing from the direction of an agricultural area with a high density of cattle feedlots and poultry and dairy farms to undetectable levels (< 1 -2 ppb or 0.70 - $0.39 \mu\text{g m}^{-3}$), when the wind was from other directions (Biermann et al., 1988). LeBel et al. (1991) reported NH_3 concentrations as high as $250 \mu\text{g m}^{-3}$ (360 ppb) during forest fires in Canada. Overall, in evaluating the significance of the air concentrations, it is important to realize that NH_3 -N accumulates in the plant tissue (after correcting for translocation). Therefore, it is not just the air concentration, but also the duration of exposure that must be considered (see Table 2).

There are diurnal variations in atmospheric NH_3 concentrations. Temperature-driven NH_3 emissions reach their maxima during noon (Georgii and Lenhard, 1978; Ryden and McNeill, 1984; McInnes et al., 1986; Grünhage et al., 1990; Hatch et al., 1990; Van der Molen et al., 1990). In contrast, NH_3 accumulation occurs at night due to atmospheric inversions. Thus, concentration maxima occur at night in areas with low NH_3 emissions (Russell et al., 1983; Alkezweeny et al., 1986; Erisman et al., 1988; Wyers et al., 1992). These considerations are important in the context of NH_3 uptake by plant shoots (see Section 3, a, below).

Variation of NH_3 concentrations during the year is typically characterized by peaks in spring and summer (Georgii and Müller, 1974; Lenhard and Gravenhorst, 1980; Levine et al., 1980; Tjepkema and Cartica, 1981; Dawson, 1984; Vermetten et al., 1985; ApSimon et al., 1987; Erisman et al., 1987; Allen et al., 1988; Kruse et al., 1989), mainly caused by application of manure and fertilizer and by the increasing temperatures.

Diurnal variations in NH_4^+ (aerosol) concentrations follow the same pattern as for NH_3 (Stevens et al., 1978; Grünhage et al., 1990; Harrison and Allen, 1990). The same holds true for seasonal variation of NH_4^+ showing maxima in spring and summer, however, with a lower amplitude compared to NH_3 (Lenhard and Gravenhorst, 1980; Tjepkema and Cartica, 1981; Erisman et al., 1987).

During 1996-1999, in West Central Alberta mean fine particulate (size $< 2.5 \mu\text{m}$) NH_4^+ concentrations varied from 0.15 to 3.10 $\mu\text{g m}^{-3}$ (maxima 0.54-3.10 $\mu\text{g m}^{-3}$) (West Central Airshed Society, Drayton Valley, Alberta). In comparison, mean fine particle NH_4^+ concentrations varied from 0.52 to 1.09 $\mu\text{g m}^{-3}$ (maxima 3.97-10.07 $\mu\text{g m}^{-3}$) at six non-urban, agricultural or rural sites in the upper Midwestern USA (Pratt and Krupa, 1985).

At two sites near Calgary, Alberta, median NH_4^+ concentrations in precipitation varied from 0.65 to 0.90 mg L^{-1} and NO_3^- levels were 1.00-1.48 mg L^{-1} (Legge et al., 1990b). In comparison median NH_4^+ values (mg L^{-1}) were at: Chalk River (Ontario) 0.19-0.30; Cormack, B (Newfoundland) 0.04-0.06; Cree Lake (Saskatchewan) 0.05-0.06; Island Lake (Manitoba) 0.08-0.09 and Port Cartier (Quebec) 0.05-0.06. For the same sites median NO_3^- values were 2.04-2.17 (Chalk River); 0.27-0.35 (Cormack B); 0.18-0.40 (Cree Lake); 0.35-0.53 (Island Lake) and 0.58-1.73 (Port Cartier) (Legge and Krupa, 1990).

2.4 Deposition

Ammonia (NH_3), and subsequently derived NH_4^+ are removed from the atmosphere both by dry and wet deposition. Dry deposition occurs by diffusion (NH_3) and Brownian motion (fine particle NH_4^+) and to a much less extent by sedimentation or impaction (coarse particles, size $> 2.5 \mu\text{m}$). It is important to note that a major portion of NH_4^+ occurs in the fine particle fraction (Finlayson-Pitts and Pitts, 1999). In contrast, wet deposition occurs by rainout (in-cloud processes) and below cloud scavenging (washout). Ammonium salts such as $[(\text{NH}_4)_2\text{SO}_4]$ are hygroscopic and act as cloud condensation nuclei.

Dry deposition is more important in regions with high NH_3 emissions and wet deposition in areas with low emissions. However, this conclusion should be moderated, because of local variabilities in the precipitation depth. According to Kociuba (1984) results of a deposition model using SO_4^{2+} as an example showed that the ratio of dry to wet deposition in Alberta was 1.86. It is important to note that frequently SO_4^{2+} and NH_4^+ are well correlated in aerosols and in precipitation and therefore, should exhibit similar tendencies in their variability (Legge and Krupa, 1990) (see also the brief narrative in Sections 2, a and b). McVehil (1990) estimated by modeling, dry to wet NH_4^+ deposition ratios of 2.4 and 3.2 at two agricultural sites near Calgary, Alberta and a ratio of 0.8 for a high elevation forested site (Fortress Mountain, Alberta). McVehil also estimated mean values for total (dry + wet) NH_4^+ deposition of 6.5 $\text{kg ha}^{-1} \text{yr}^{-1}$ and NO_3^- deposition of 11 $\text{kg ha}^{-1} \text{yr}^{-1}$ for southern Alberta.

Although comparisons between predicted and measured deposition values may be in good agreement (Derwent et al., 1989), model calculations may be quite erroneous because of several uncertainties in the input data. This is particularly true for emission data and for dry deposition velocities (V_d) which are highly variable depending among others on daytime-nighttime micrometeorological conditions such as wind characteristics, radiation, temperature, humidity,

pH of the receptor and roughness of the surface (e.g., short grass, broad-leaved trees, conifers). Some data on V_d for NH_3 and NH_4^+ are listed in Table 1, suggesting that a reasonable range of V_d is $0.3\text{--}3\text{ cm s}^{-1}$ for NH_3 and values one order of magnitude lower for fine particle NH_4^+ .

Furthermore, most deposition models do not reflect the high local scale variation mainly caused by differences in the receptor qualities of the canopies. Interception during dry deposition may significantly increase total NH_y deposition within plant canopies. In unpolluted stands, NH_y uptake within the plant canopy layer causes concentrations of NH_4^+ in canopy deposition (throughfall plus stemflow) to be lower than concentrations in bulk deposition (Verry and Timmons, 1977; Lindberg et al., 1986; Heil et al., 1987b, 1988, 1989). In polluted areas, canopy deposition is significantly greater than bulk deposition above the canopy (Van Breemen et al., 1982; Ivens et al., 1989; Van Dam et al., 1991; Bobbink et al., 1992a). Some data for different canopies are given in Table 2. Thus, regional scale models may significantly underestimate deposition to ecosystems with large canopy surfaces.

In addition, agro-ecosystems intensively fertilized with N may act as a source for NH_3 rather than as a sink. Grünhage et al. (1992) measured NH_3 flux of a fertilized grassland ($240\text{ kg N ha}^{-1}\text{ yr}^{-1}$) by micrometeorological methods and found that annual NH_3 budget to be negative, i.e., NH_3 was emitted from the system on an annual time scale. Thus, if agricultural areas enriched with N are sources rather than sinks for NH_y ($\text{NH}_3 + \text{NH}_4^+$), deposition to an N poor ecosystem may be significantly higher than suggested by average deposition values from model calculations.

3.0 EFFECTS OF NH_3 AND NH_4^+ (NH_y) ON VEGETATION

Both anthropogenic NH_3 and NH_4^+ derived from it, significantly influence N cycling in ecosystems (Fangmeier et al., 1994; Fenn et al., 1998). Since under field conditions the chronic effects of NH_3 and NH_4^+ are often difficult to distinguish, the two are considered together as NH_y .

Fangmeier et al. (1994) provided a state of the science review of the effects of NH_y on plants. The current knowledge of the effects of NH_y on plants is based on studies using a number of different approaches. These include experimental designs using artificial exposures to NH_3 or NH_4^+ either in controlled environment chambers, greenhouses, closed or open-top field chambers and chamber-less field studies where the physical and the chemical (pollution) climate are not controlled. For details on various exposure methods, the reader is referred to Manning and Krupa (1992). A summary of studies published within the past 20 years that provide information about the effects of NH_3 on plants is given in Table 3. In that table, results from fumigation experiments with known concentrations of NH_3 are included. Additionally, results of some field studies are provided where NH_3 was considered to be the major air pollutant, because of the vicinity of the study plots to the emission sources. The data summarized in Table 3 are listed according to the response parameters measured in the test plants and provide background information for the following sections on the NH_y effects on plants.

According to Fangmeier et al. (1994), NH_y effects on plants depend on several processes as illustrated in Figure 1: (a) uptake, (b) detoxification/assimilation, (c) development of injury when the amount of uptake exceeds detoxification, (d) metabolic changes related to detoxification/assimilation and (e) secondary effects following NH_y uptake and successful detoxification.

3.1 Uptake of NH_y by Shoots and by Roots

3.1.1 NH_3 (shoots)

Atmospheric NH_3 enters the leaves of higher plants almost exclusively through the stomata and is dissolved in the water film of the mesophyll cells to form NH_4^+ (Van Hove et al., 1987a). NH_3 flux into bean leaves (*Phaseolus vulgaris*) increased linearly with NH_3 concentration, and no mesophyll resistance to NH_3 uptake could be detected (Van Hove et al., 1987b). The cuticle was found to be nearly impermeable for NH_3 (Van Hove et al., 1987a,b, 1989b). Thus, NH_3 uptake directly follows stomatal conductance and therefore depends on the microclimate (radiation, air temperature, relative humidity, air turbulence and soil moisture availability) (Rogers and Aneja, 1980; Van Hove et al., 1990), internal CO_2 concentration, and plant water status (Hutchinson et al., 1972; Harper et al., 1989).

The driving force for NH_3 uptake is its concentration gradient between ambient air and the mesophyll tissue. As long as ambient NH_3 concentrations exceed the mesophyll concentration (compensation point), NH_3 uptake by the shoot will occur. However, at background ambient concentrations (approximately $1\text{--}10\ \mu\text{g m}^{-3}$ (1.44–14.4 ppb), i.e., 0.15–1.5 mPa), internal

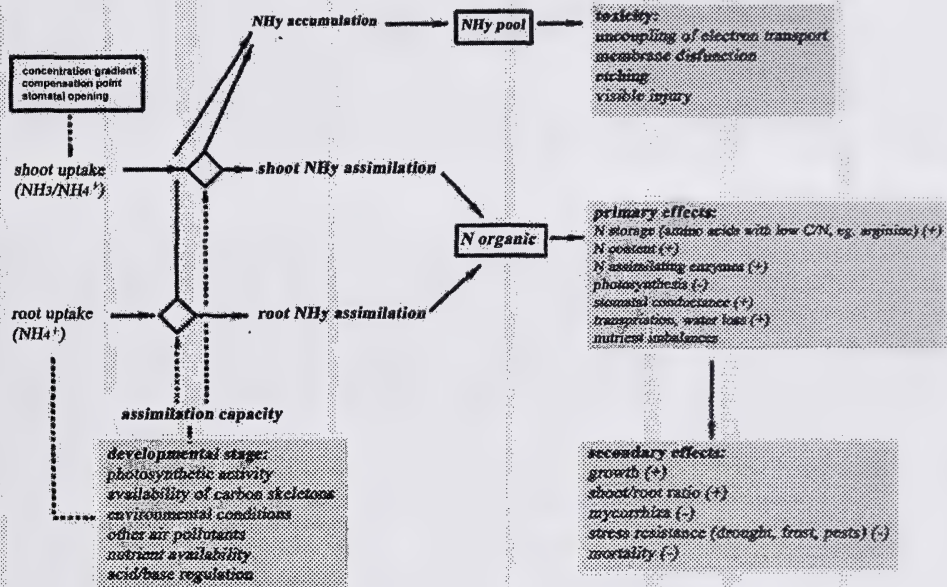


Figure 1 Pathways and factors governing the effects of NH_3 on plants. Source: modified from Fangmeier et al. (1994)

mesophyll NH_3 concentration may exceed ambient levels and cause emission of NH_3 from the plant. Internal mesophyll NH_3 concentration as is, approximates 0.25 mPa at 'normal' metabolism in beans (Farquhar et al., 1980) and may increase significantly during senescence, because of the destruction of proteins and amino acids (Stewart et al., 1987; Raven, 1988) or if plants are very well supplied with N through the use of fertilizers (Harper et al., 1987; Parton et al., 1988; Morgan and Parton, 1989; Schjoerring, 1991; Schjoerring et al., 1991). Calculations by Raven (1988) showed that at background concentrations NH_3 uptake by shoots may only play a minor role in N-nutrition of higher plants. However, elevated concentrations may significantly contribute to N-nutrition, as was shown by Faller (1972) in experiments with up to 1.6 mg m^{-3} (2.3 ppm) NH_3 . In that case growth of sunflower continued to occur if NH_3 was the only nitrogen source. In experiments with *Lolium multiflorum* (ryegrass), foliar NH_3 uptake at $520 \mu\text{g m}^{-3}$ (748 ppb) supplied 47.3% of total plant N at fertilization with $100 \text{ mg } ^{15}\text{NO}_3\text{-N kg}^{-1}$ and 35.2% at $200 \text{ mg } ^{15}\text{NO}_3\text{-N kg}^{-1}$ dry soil (Lockyer and Whitehead, 1986). Pérez-Soba and Van der Eerden (1993) exposed *Pinus sylvestris* L. (Scots pine) saplings to 0 and $50 \mu\text{g m}^{-3}$ (72 ppb) NH_3 and fertilized the saplings with $(\text{NH}_4)_2\text{SO}_4$ in the range of 0-200 $\text{kg ha}^{-1} \text{ yr}^{-1}$. After four months of plant growth they found an increase in the N content of the needles of 49% by NH_3 , while the increase due to fertilization with 200 $\text{kg ha}^{-1} \text{ yr}^{-1}$ was only 8%.

3.1.2 NH_4^+ (shoots)

NH_4^+ is accumulated on leaf surfaces both by dry and wet deposition (Gmur et al., 1983; Van Hove et al., 1989b; Bobbink et al., 1992a). Some comparisons between bulk deposition and throughfall of different canopies (grassland, heathland, forests) showed that an uptake of NH_4^+ by the canopies was accompanied by a release of K^+ , Mg^{2+} , and Ca^{2+} (Lovett et al., 1985; Heil et al., 1987a, 1988; Ivens et al., 1987; Roelofs et al., 1987a; Alenas and Skärby, 1988; Leonardi and Flückiger, 1989; Garten and Hanson, 1990; Van Dam et al., 1991; Bobbink et al., 1992a). Foliar uptake of NH_4^+ is generally higher in grassland and heathland than in forest trees. The question of how NH_4^+ enters the leaves has not yet fully been answered. Wilson (1992) exposed branches of *Picea abies* (Norway spruce) and *Pinus sylvestris* (Scotch pine) to artificial rain solutions containing NH_4^+ or NO_3^- , and concluded that uptake was due to diffusion rather than H^+ or base cation exchange as commonly accepted. That conclusion should be tempered, because as opposed to solutions or precipitation, fine particle (size $< 2.5 \mu\text{m}$) deposition of NH_4^+ follows Brownian motion and not diffusion. Nevertheless, fine particles enter the leaf through stomata, same as NH_3 (Chevone et al., 1986), although that process may result in stomatal clogging.

3.1.3 NH_4^+ (roots)

Normally root uptake of NH_3 does not occur since the NH_3 deposited to the soil is readily dissolved to yield NH_4^+ . NH_4^+ in soils is less mobile than NO_3^- , but is easily accessible to plants under most conditions. The ratio of NO_3^- to NH_4^+ uptake depends on the pH of the soil (Bergback and Borg, 1989; Henry and Raper, 1989; Vessey et al., 1990), rooting zone temperature (Kafkafi, 1990; MacDuff and Jackson, 1991), rooting depth (Gijsman and De Willigen, 1991), mycorrhizal formation (Martin et al., 1986; Finlay et al., 1988; Marschner et al., 1991), ion concentration and the dominant type of nitrogen assimilation pathway of the plant species (Pearson and Stewart, 1993). NH_4^+ may prevent NO_3^- uptake and vice versa (Ullrich, 1987; Lee and Drew, 1989; Deignan and Lewis, 1988).

Uptake of NH_4^+ leads to acidification of the rooting zone, since it is exchanged with protons exuded by the roots (Tamm, 1991). Another problem arises from competition in the uptake between NH_4^+ and other cations such as K^+ (Lips et al., 1987; Vale et al., 1987). K^+ deficiency may occur in plants provided with NH_4^+ as sole N-source (Kinzel, 1982; Roelofs et al., 1985). NH_4^+ uptake via the roots may be reduced if shoot uptake of NH_3 occurs. Pérez-Soba and Van der Eerden (1993) found decreased NH_4^+ sorption in roots of *Pinus sylvestris* (Scotch pine) when the shoots were fumigated with NH_3 .

3.2 Assimilation and Detoxification of NH_3

NH_3 taken up by the shoots readily reaches equilibrium with NH_4^+ in the water film of the mesophyll tissue. There, NH_4^+ strongly dominates NH_3 and is assimilated, whereas NH_4^+ taken up from the soil is metabolized in the roots. Both in the roots and in the shoots, NH_4^+ assimilation takes place via the enzymes glutamine synthetase/glutamate synthase (GS/GOGAT) system (Lea and Miflin, 1974; Lewis et al., 1987; Stewart et al., 1987; Tischner, 1987; Valpuesta et al., 1987; Wallsgrove, 1987) (Figure 2). Although glutamate dehydrogenase is assumed to be an alternative for GS/GOGAT system (Srivastava and Singh, 1987), generally that enzyme plays a minor role in the assimilation of NH_3 (Rhodes et al., 1989).

Two isoenzymic (isoenzymes are groups of enzymes that are very similar in their catalytic properties, but may be differentiated by the variations in their physical properties) forms of glutamine synthetase (GS) are found in plants: one common in chloroplasts of all species investigated and one in the cytoplasm of some species. The latter isoenzyme is thought to be responsible for NH_4^+ assimilation derived from photorespiration or from arginine decomposition by arginase or transaminases (Tischner, 1987). Glutamate synthase (GOGAT) exists in three isoenzymic forms dependent respectively on NADH, NADPH or ferredoxin that are found in the chloroplasts and in root cell plastids.

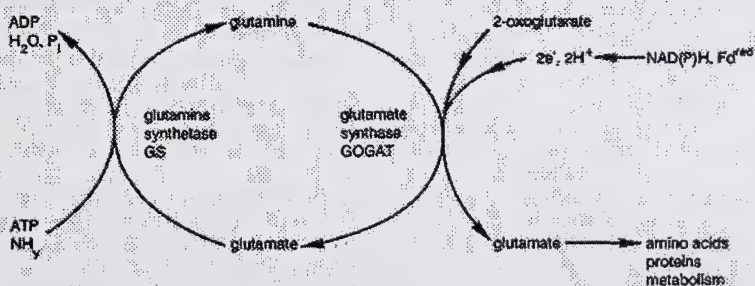


Figure 2 Glutamine synthetase (GS) - Glutamate synthase (GOGAT) pathway of NH_3 assimilation in plants

3.3 Metabolic Changes Due to NH_y Assimilation and Detoxification

NH_y detoxification may lead to significantly increased contents of organic nitrogen.

In *Calluna vulgaris* (heather) and *Deschampsia flexuosa* (hair-grass), the nitrogen content increased four-fold after exposure to 0.1 mg m^{-3} (144 ppb) NH_3 for 38 weeks (Van der Eerden et al., 1991). Increased N contents were also found in conifers both in fumigation experiments (Van der Eerden et al., 1989, 1992; Dueck et al., 1990) and in field studies near NH_3 sources (Van Dijk and Roelofs, 1988; Hofmann et al., 1990; Heinsdorf and Krauß, 1991). That was also true in tomato (*Lycopersicon esculentum*) and clover (*Trifolium pratense*) exposed to poultry farm emissions (Hauk et al., 1990). Increases in N content in conifer needles proved to be age dependent. The highest increases were found in current year needles, because of higher stomatal conductivity and higher metabolic activity in the younger tissue (Van der Eerden et al., 1989, 1992; Dueck et al., 1990; Van der Eerden and Pérez-Soba, 1992).

If NH_y uptake exceeds the assimilation capacity, NH_y will accumulate in the tissue resulting in toxic effects. Tissue accumulation of NH_y was observed in lettuce (*Lactuca sativa* var. *capitata*) and tomato following exposures to acute NH_3 concentrations, in controlled conditions (Van der Eerden, 1982; Hülsenberg, 1990) and in highly polluted conifer stands near livestock farms (Tesché and Schmidtchen, 1978; Heinsdorf and Krauß, 1991). Hofmann et al. (1990) distinguished three nutritional states in Scotch pine (*Pinus sylvestris*) according to the needle N content: (a) 'deficient', 1.0-1.8%, corresponding to the situation normally found in natural pine stands; (b) 'saturation', 1.8-2.35%, providing maximum growth and representing the physiological optimum (but not the ecological optimum which is below 1.8%); and (c) 'excess', 2.35-3.5%, causing growth reductions and in the long-term, injury. Stand stability decreases even at 2.0% nitrogen content.

Detoxification of NH_y is most effective if carbon skeletons are consumed as little as possible, i.e., if the nitrogen is stored in compounds with low C/N ratios. Indeed, alterations in the amino acid composition of plants exposed to NH_y reflect the attempts of the plants to detoxify NH_y most economically. Arginine with a C/N ratio of only 1.5 is one of the amino acids most significantly increased (up to 25-fold) when plants are exposed to NH_y (Van Dijk et al., 1992). Such results were obtained in the case of *Pinus sylvestris* fumigated with NH_3 (Pérez-Soba et al., 1990; Van der Eerden et al., 1990a) or growing close to fur farms (Pietilä et al., 1991), and with *Calluna vulgaris* near to a liquid manure storage facility (Steubing et al., 1991). In the latter experiment, however, *Deschampsia flexuosa* responded with increased concentrations of glutamine (C/N = 2.5) and asparagine (C/N = 2), but not arginine. Van Dijk and Roelofs (1988) found a 25-fold increase in arginine in needles of *Pinus sylvestris* injured from agricultural NH_y . According to Roelofs et al. (1987a,b) yellowing at the base of the youngest needles corresponds to extremely high arginine concentrations. Another amino acid, proline, is often increased by exposure to NH_y (Van Dijk et al., 1992). An elevated proline concentration is assumed to indicate drought stress.

In most cases, plants exposed to NH_y show increased concentrations of soluble proteins, as in *Picea abies* (Zedler et al., 1986), *Pinus sylvestris* (Pietilä et al., 1991), *Deschampsia flexuosa* and *Calluna vulgaris* (Steubing et al., 1991). Pietilä et al. (1991) reported alterations in the protein

spectrum of *Pinus sylvestris* needles. Proteins with molecular weights 30, 38, 50, and 65-90 kd were absent in plants growing close to fur farms, probably causing reduced frost hardness.

Besides alterations of specific amino acids or protein fractions, concentrations of most cellular compounds containing nitrogen tend to be increased. This also holds true for pigment contents. As long as the tissue is not injured, chlorophyll concentrations in plants exposed to NH_3 increase, as in *Pinus sylvestris* (Pérez-Soba et al., 1990; Van der Eerden et al., 1990a), *Deschampsia flexuosa* and *Calluna vulgaris* (Steubing et al., 1991).

If NH_3 applied via the shoot has to be detoxified, the enzymes responsible for assimilation, i.e. GS/GOGAT, should be more active. In the few experiments where glutamine synthetase activity in shoots was measured after NH_3 exposure, increased GS activities were indeed observed in *Pinus sylvestris* (Pérez-Soba et al., 1990; Van der Eerden et al., 1990a) and in *Deschampsia flexuosa*, but not in *Calluna vulgaris* (Steubing et al., 1991).

NH_3 uptake *per se* may lead to nutrient imbalances by increased nitrogen content and by growth increments accompanied by insufficiently increased uptake of nutrients other than nitrogen. This effect may be further increased by competition between root NH_3 uptake and uptake of other cations such as K^+ and by leaching of K^+ , Mg^{2+} and Ca^{2+} during shoot NH_4^+ uptake. However, no ion leaching was found when shoots of *Pseudotsuga menziesii* (Douglas fir) and *Calluna vulgaris* were fumigated with NH_3 (Van der Eerden et al., 1990a, 1992). Thus, variations in nutrient relations occur following NH_3 exposure. Current year needles of *Pseudotsuga menziesii* fumigated with NH_3 showed decreased contents of K^+ and PO_4^- (Pérez-Soba et al., 1990), whereas Ca^{2+} and Mg^{2+} contents remained unchanged and no alteration in K^+ , PO_4^- , Ca^{2+} or Mg^{2+} was detected in the previous year needles. Even if the nutrient contents remain unchanged after NH_3 exposure, as in *Pinus sylvestris* (Van der Eerden and Pérez-Soba, 1992), the N/ion ratios are altered since N contents increase after NH_3 uptake. N/K, N/Mg and N/P ratios increased both in current and previous year needles in *Pseudotsuga menziesii* exposed to NH_3 , however, the effects were more pronounced in current year needles (Van der Eerden et al., 1989, 1992). Field surveys in pine forests surrounded by intensive livestock operations showed the same type of nutrient imbalances (Van Dijk and Roelofs, 1988). Van Dijk et al. (1990) found mortality of up to 100% after a seven-month treatment of several conifer species with artificial rain containing $5,000 \mu\text{mol L}^{-1}$ $(\text{NH}_4)_2\text{SO}_4$. They suggested that K^+ deficiency, rather than Al^{3+} toxicity, may have been the major cause of this mortality.

3.4 Changes in Leaf Gas Exchange Following Exposure to NH_3

Leaves of *Populus euramericana* (poplar) showed increased stomatal conductance after NH_3 exposure at $100 \mu\text{g m}^{-3}$ (144 ppb) for 6 or 8 weeks (Van Hove et al., 1989a). At the same time, the CO_2 assimilation rate, P_{max} , in particular was increased. Increased photosynthesis was also reported for *Pinus sylvestris* at exposures to $240 \mu\text{g m}^{-3}$ (346 ppb) NH_3 (Van der Eerden et al., 1990b; Van der Eerden and Pérez-Soba, 1992). Van Hove et al. (1989a) assumed that higher demand for carbon skeletons resulting from NH_3 assimilation was responsible for increased CO_2 fixation and increased stomatal conductance to be regulated by internal CO_2 concentration, whereas NH_3 itself had no direct influence on stomatal conductance. Thus, NH_3 uptake may cause an autocatalytic increase of further NH_3 flux into the leaves by inducing stomatal opening

via the internal CO₂ level, as long as photon flux density is sufficient for equivalent photosynthesis (Van der Eerden and Pérez-Soba, 1992).

Whether or not dark respiration responds to NH₃ remains unclear. Van Hove et al. (1989a, 1991) did not observe NH₃ effects on dark respiration of *Populus euramericana*, whereas *Pinus sylvestris* showed significantly enhanced dark respiration after fumigation with NH₃ (Van der Eerden and Pérez-Soba, 1992).

Stomatal opening induced by NH₃ caused higher transpiration rates and thus, altered water relations. Transpiration increased significantly in *Pinus sylvestris* saplings exposed to NH₃ in climate chambers and branch water potential decreased (i.e., became more negative) after drought stress for 10 days, compared to the control plants (Van der Eerden et al., 1990b; Van der Eerden and Pérez-Soba, 1992). Similar results have been obtained by Dueck et al. (1990), by using open-top chambers to expose *Pinus sylvestris* saplings to NH₃.

3.4.1 Effects of NH₃ on Epicuticular Waxes

NH₃ entering the leaves via the stomata may affect mesophyll processes, but NH₃ may also directly alter the cuticle. Needles of *Pseudotsuga menziesii* (Douglas fir) exposed to NH₃ in climate controlled growth chambers (Van der Eerden et al., 1992), in open-top chambers (Thijse and Baas, 1990) and tree stands polluted with NH₃ (Thijse and Baas, 1990) showed erosion of the crystalline wax structures. Erosion also occurs naturally during needle aging, however, it was enhanced by NH₃ in the experiments. In contrast, no significant effects were found on wax erosion (e.g., building of amorphous wax) in *Pinus sylvestris* needles exposed to NH₃ at 60 or 100 µg m⁻³ (86 or 144 ppb) for nine months (Bacic et al., 1992) or in *Populus euramericana* leaves fumigated for seven weeks at 64 µg m⁻³ (92 ppb) (Van Hove et al., 1991).

Although experimental results show that NH₃ can damage the epicuticular wax layer, that effect is difficult to assess under field conditions, because of natural fluctuations in growth, aging, wax re-crystallization, presence of other air pollutants and stress factors and high intra-species variation.

3.4.2 Factors Determining the Toxicity of NH₃

NH₃ may: (a) function as an electron acceptor, thus causing uncoupling of electron transport along membranes (Losada and Arnon, 1963); (b) saturate membrane lipids, thus causing membrane dysfunction (Van der Eerden, 1982) and (c) cause direct leaf etching and necrosis (death) at very high concentrations (Van der Eerden et al., 1990c). Since NH₃ may not be stored in the tissues without damage, plants readily try to assimilate NH₃ to form organic nitrogen compounds. Thus, primary toxicity of NH₃ arises as soon as uptake exceeds assimilation capacity.

The plant's capacity to detoxify (i.e., to assimilate) NH₃ depends on several internal and external parameters. Internally, NH₃ assimilation requires carbon skeletons, energy (ATP), and reduction equivalents (NAD(P)H, ferredoxin). Thus, high rates of NH₃ assimilation may be expected at growth stages with high metabolic activity; generally external conditions (irradiation, temperature, water supply) favoring high rates of photosynthesis.

The influence of the developmental stage of the tissue on NH_3 detoxification capacity is important. According to Tesche and Schmidtchen (1978) NH_3 pollution near livestock farms resulted in shedding of older conifer needles before the younger needles were injured. Greenhouse fumigations with acute concentrations of NH_3 (2-2.8 mg m^{-3} or 2.9-4.0 ppm) caused injury first to the older needles of *Pinus sylvestris*, *P. nigra* (Austrian pine) and *P. mugo* (Mugo pine) (Ewert, 1979). Age dependent reactions of conifer needles were also found at NH_3 concentrations lower than the acute levels. Increased N content after NH_3 fumigation were only observed in the current year needles of Douglas fir (*Pseudotsuga menziesii*) (Van der Eerden et al., 1989, 1992) and *Pinus sylvestris* (Dueck et al., 1990). Likewise, needle biomass increased only in current year flushes of *Pinus sylvestris* fumigated with NH_3 (Van der Eerden et al., 1990b; Van der Eerden and Pérez-Soba, 1992).

At conditions limiting photosynthetic capacity and thus, availability of carbon skeletons and energy, NH_3 proved to be more toxic than under more favorable conditions. For example, Van der Eerden (1982) exposed tomato (*Lycopersicon esculentum*) to 2 mg m^{-3} (2.9 ppm) NH_3 and found foliar injury after 24 h in the dark, but not in the light. Similar effects were observed at low temperatures limiting metabolism in general and thereby reducing NH_3 assimilatory capacity. Conifers exposed to NH_3 in the field near a pig farm or fumigated in open-top field chambers were injured only during wintertime (fumigation concentration: 0.25 mg m^{-3} or 360 ppb) and not in the spring (fumigation concentration: 0.54 mg m^{-3} or 778 ppb) (Van der Eerden, 1982).

The potential of NH_3 to cause metabolic disturbance is also a function of the type of nitrogen nutrition of a particular species. Pearson and Stewart (1993) developed a concept called the 'leaf metabolic vitality theory' to divide plants into groups with differing susceptibility to NH_3 . This was based on their leaf acid-base regulation, which is related to the type of nitrogen nutrition. Plants may be roughly divided into three groups: those preferring NO_3^- , those preferring NH_4^+ , and those using both NO_3^- and NH_4^+ . Most fast growing annual species, among them most agricultural crops (Kinzel, 1982; Malhi et al., 1988), and fast growing pioneer trees such as *Betula* spp. (birch), *Populus* spp. or *Sambucus nigra* (black elderberry) prefer NO_3^- (Pearson and Stewart, 1993), whereas slow growing perennial species mainly prefer NH_4^+ . *Ericaceae* (e.g., *Calluna* spp.; *Erica* spp., and *Vaccinium* spp., bilberry, blueberry, etc.), conifers, climax species among broad-leaved trees such as *Quercus* spp. (oak), *Fagus sylvatica* (beech), and *Carpinus betulus* (hornbeam), and an exception among crops, rice (*Oryza sativa*) (because of the anaerobic soil conditions) belong to the latter group (Van den Driessche and Dangerfield, 1975; Kinzel, 1982; Blacquièrre et al., 1988; Magalhaes and Huber, 1991; Pearson and Stewart, 1993). Plants preferring NO_3^- may further be divided into those assimilating nitrate in the roots, in the shoots, or both in the roots and shoots.

Raven (1988) calculated that assimilation of 1 mol NH_4^+ , irrespective of root or shoot uptake, forms 1.33 mol H^+ , and NH_3 forms 0.33 mol H^+ , in the synthesis of core metabolites. Taking into account the assimilation of S from sulfate and P from phosphate resulting in production of some OH^- , excess H^+ production is 1.22 mol H^+ , when 1 mol NH_4^+ is assimilated, and 0.22 mol H^+ when 1 mol of NH_3 is assimilated (Raven, 1988). On the other hand, 0.78 mol excess OH^- is yielded when 1 mol NO_3^- is reduced to form amino groups (Raven, 1988).

Plants may easily get rid of H^+ resulting from NH_4 uptake and assimilation, if these processes take place in the roots, by excreting H^+ into the soil (however, with the consequence of further increasing the acidity of the rooting zone). On the other hand, it seems unlikely that H^+ may readily be removed from shoots (Raven, 1988; Pearson and Stewart, 1993). Thus, even small amounts of H^+ from shoot NH_4 uptake and assimilation may disturb acid-base balance in leaves (Pearson and Stewart, 1993). Those species preferring nitrate uptake and transport into the leaves for assimilation, however, may buffer significant amounts of H^+ by OH^- production from NO_3^- assimilation and are expected to be more tolerant to foliar uptake of NH_4 (Pearson and Stewart, 1993).

3.5 Direct Toxicity of NH_4 and Visible Foliar Injury

Accidental releases of NH_3 from industrial processes or during its transport are known. In most of these cases, the concentrations will be extremely high and the exposure time will be very short. In these episodes the dominant cause of injury is a direct chemical 'etching' of the foliage (Temple et al., 1979; De Temmerman, 1980). Table 4 provides a listing of plants considered to be sensitive, intermediate or tolerant to NH_3 exposures, based on foliar injury symptoms. The order of sensitivity among plant species, for the types of exposures resulting in injury symptoms, is different from the order at lower concentrations over longer periods. For instance, for short-term exposures conifers are highly resistant (Temple et al., 1979), while for longer exposures they are relatively sensitive (Van der Eerden, 1982).

Generally, the assimilation capacity of the plant species determines the degree of injury. If the assimilation capacity is not sufficiently high to detoxify NH_4 , acute (visible) injuries may occur. On broad-leaved plants acute exposures to anhydrous NH_3 will result in the death of the leaf tissue between the veins (inter-veinal necrosis) (Figures 3 and 4). This can be easily confused with similar symptoms caused by acute exposures to sulphur dioxide (SO_2) (Krupa and Legge, 1999b; also see Jacobson and Hill, 1970; Flagler, 1998). Several cereals and grasses show chlorotic (yellow) and necrotic (dark tan to brown) inter-veinal streaking.

In Europe, field observations have been made by a number of investigators, mostly on trees in the vicinity of NH_3 sources such as livestock farms, manure storage facilities or fertilizer plants (Kühne, 1966; Garber and Schürmann, 1971; Scholl, 1975; Ewert, 1978a,b; Hunger, 1978; Tesche and Schmidtchen, 1978; Schulz, 1980; Rudolph, 1981; Van der Eerden et al., 1981; Van der Eerden, 1982; Sun, 1989; Kaupenjohann et al., 1989; Kaupenjohann, 1990; Hofmann and Heinsdorf, 1990; Heinsdorf and Krauß, 1991). Conifers near livestock farms usually respond to NH_3 by needle necrosis (death) starting at the tips of the oldest needles, subsequently with needle loss and finally with the death of the tree. In the former GDR (East Germany), in the vicinity of huge pig farms with up to 200,000 pigs, forest decline areas of 2,000 ha attributable to NH_3 have been observed (Hofmann and Heinsdorf, 1990). Roelofs et al. (1987a,b) defined four types of visible NH_4 injury on *Pinus sylvestris*: (a) red or brown needle discolouration (insufficient NH_4 detoxification); (b) yellowing of needles, occurring more frequently in older needles (K^+ and/or Mg^{2+} deficiency); (c) yellowing of the youngest needles, most pronounced at the needle base (extremely high arginine content); and (d) occurrence of fungal or insect diseases (nutrient imbalance).

Controlled exposures in greenhouses with acute NH_3 concentrations ($2\text{--}28\text{ mg m}^{-3}$) showed that injury symptoms differ with plant species (Ewert, 1979). Broad-leaved trees mainly displayed black discoloration of the leaves, whereas conifers mostly displayed brown needle necrosis. Van der Eerden (1982) described sharply bordered necrotic tips of older needles of *Taxus baccata* (yew) to be specific for NH_3 . However, in most cases leaf injury from acute NH_3 concentrations may not easily be distinguished from symptoms caused by other stresses (Van der Eerden, 1982).

Visible symptoms observed on plant organs other than leaves include reduced flowering in *Arnica montana* (mountain tobacco) after fumigation with NH_3 at 0.053 mg m^{-3} (76 ppb) for 15 months (Van der Eerden et al., 1991), reduced number of flowers by 50% in *Petunia hybrida* (petunia) exposed to acute NH_3 concentrations ($> 2\text{ mg m}^{-3}$ or $> 2.9\text{ ppm}$) for two weeks (Van Haut et al., 1979) and empty ear development in oat (*Avena sativa*) exposed to poultry farm emissions containing NH_3 at $2.3\text{--}3.9\text{ mg m}^{-3}$ ($3.3\text{--}5.6\text{ ppm}$) (Hauk et al., 1990).

Epiphytic lichens growing on tree trunks can be used as biological indicators of acute anhydrous NH_3 exposures. Lichens contain complex organic acids (lichenic acids). These acids react with anhydrous NH_3 , conferring a purple coloration to the lichens within 1-2 days after exposure (Figure 4 B).



Figure 3 (A). Row of table beet (*Beta vulgaris*) exposed to acute (relatively high) anhydrous NH_3 concentrations due to an industrial malfunction. (B). Close-up of a table beet leaf showing acute response to anhydrous NH_3 . Note the death of the leaf tissue (brown areas) between the veins. These symptoms are very similar to those induced by acute exposure to SO_2



Figure 4 (A) Cherry tomato (*Lycopersicon esculentum* var. *cerasiforme*) showing acute response (white bleached areas between the veins) to anhydrous NH_3 . (B). Epiphytic lichens on the trunk of an oak tree exhibiting purple colouration due to acute exposure to anhydrous NH_3 . This response can be used as a biological indicator of NH_3 pollution

4.0 SECONDARY EFFECTS OF NH_y UPTAKE AND ASSIMILATION ON VEGETATION

4.1 Growth Responses

One of the most obvious plant responses that might be regarded as 'secondary' effect after NH_y assimilation, is enhanced growth. This should not be surprising since nitrogen must be regarded as a limiting factor (in the sense of biomass production) for plant growth in most (natural) habitats. Enhanced growth has been observed in many experiments as long as the NH_y concentrations were not toxic. At acute (toxic) NH_3 concentrations, however, growth is depressed (Van Haut et al., 1979; Van der Eerden, 1982; Hülsenberg, 1990).

Whenever increased growth is observed after NH_y application that is mainly due to the shoot growth response. Root growth increases only a little or at least less than shoot growth, leading to higher shoot/root ratios (Encke, 1986). This has been shown for both gaseous NH_3 and NH_4^+ in precipitation. Increased shoot/root ratios were observed following NH_3 exposures in several species such as *Agrostis capillaris* (bentgrass), *Arnica montana* (Van der Eerden et al., 1990a), *Calluna vulgaris* (Van der Eerden et al., 1990a,c, 1991), *Deschampsia flexuosa* (Dueck et al., 1991), *Potentilla erecta* (tormentil), *Viola canina* (dog violet) (Van der Eerden et al., 1990a) and *Pinus sylvestris* (Van der Eerden et al., 1990b; Van der Eerden and Pérez-Soba, 1992). After a seven-month treatment with artificial rain containing $(\text{NH}_4)_2\text{SO}_4$, Van Dijk et al. (1990) found no influence on the total biomass production, but an increase in the ratios of shoot/root and coarse/fine roots. Field observations showed that the fine root content in the soil of pine forests decreased close to pig farms (Hofmann and Heinsdorf, 1990).

Competition between root growth and NH_y assimilation as sinks for carbon skeletons is likely responsible for altered shoot/root ratios after NH_y uptake. Shoot uptake of NH_y will keep photosynthetic primary products in the shoot, whereas root uptake of NH_y will increase the demand for NH_4^+ acceptor molecules and inhibit the synthesis of structural root compounds and may even lead to conversion of structural compounds into NH_4^+ acceptor molecules (Lewis et al., 1987).

Thus, enhanced growth caused by NH_y uptake may not necessarily be regarded as beneficial but rather as detrimental, if other effects such as decreased resistance to environmental stress as described in the following section are considered. Some experimental findings indicate that growth enhancement may turn into increased mortality of plants at a later developmental stage or during environmental stress. Dueck (1990) found a 20% reduction of the survival rate of *Calluna vulgaris* seedlings that had been fumigated with NH_3 at 53 or 105 $\mu\text{g m}^{-3}$ (76 or 151 ppb) for eight months. Survival of *Antennaria dioica* (cat's-foot) was reduced by 30% at the same concentrations applied for 16 months and *Arnica montana* by 50% (Van der Eerden et al., 1991). The authors explained the high mortality of *Arnica montana* as due to an altered shoot/root ratio, resulting in a higher susceptibility to environmental stresses.

4.2 Resistance to Stress

4.2.1 Drought Resistance

Van der Eerden and Pérez-Soba (1992) exposed *Pinus sylvestris* saplings to NH_3 at up to $240 \mu\text{g m}^{-3}$ (346 ppb) for three months. Water loss and transpiration drastically increased in fumigated plants and branch water potential decreased (i.e., became more negative) significantly after withholding water for 10-14 days from the plants. Similar results were obtained with *Calluna vulgaris* plants which experienced irreversible drought injury after fumigation with $240 \mu\text{g m}^{-3}$ (346 ppb) NH_3 and drought stress for 10 days, whereas controls and plants exposed to lower NH_3 concentrations were able to recover from drought stress (Van der Eerden et al., 1991).

That NH_3 may decrease the resistance to drought stress may be explained by at least two mechanisms (Fangmeier et al., 1994). First, the demand for carbon skeletons to assimilate NH_3 increases CO_2 uptake and thus, stomatal opening and water loss. Secondly, since shoot growth is more enhanced by NH_3 than root growth, water supply from the roots may easily become insufficient during periods of drought.

4.2.2 Frost Resistance

Several studies with conifers suggest that NH_3 may reduce frost hardiness. NH_3 at $105 \mu\text{g m}^{-3}$ (151 ppb) applied in open-top chambers increased frost sensitivity (measured as electrolyte leaching) of *Pinus sylvestris* needles exposed at -10°C (Dueck et al., 1990; Van der Eerden et al., 1990b). Dueck et al. (1990) believe that NH_3 at low to moderate concentrations prolongs the growth phase in autumn and causes winter hardiness to develop too late, which may have detrimental consequences if first frost periods occur early in the year. These findings are supported by field observations by Pietilä et al. (1991), who reported dieback of *Pinus sylvestris* during the winter in the vicinity of fur farms and by De Temmerman et al. (1987) who observed that frost injury significantly contributed to *Pinus sylvestris* dieback in Belgium and such injury was most pronounced near NH_3 sources (livestock management, fields intensively sprayed with liquid manure). Misting of red spruce (*Picea rubens*) with $(\text{NH}_4)_2\text{SO}_4$ for seven months decreased frost hardiness at the end of October (Cape et al., 1991).

4.2.3 Insect Pests

Most insect pests may attack their hosts more successfully at nitrogen levels in the host tissue higher than those usually found under field conditions. Increased nitrogen content caused by NH_3 uptake may thus weaken the host defense against pests. In addition, altered foliar C:N ratios in the plant may influence herbivory, as with N fertilization (Krupa et al., 1998). Pest/host interaction at elevated NH_3 pollution has been studied intensively with the heather beetle (*Lochmaea suturalis*), the larvae of which prey on leaves of *Calluna vulgaris*. Van der Eerden et al. (1991) exposed *Calluna vulgaris* to NH_3 at concentrations between 4 and $107 \mu\text{g m}^{-3}$ (5.8 and 154 ppb) for 12 months and fed the beetle larvae with leaves harvested from those plants. There was an increase in the number of larvae reaching the third (last) and most injurious instar (growth stage) with increasing pre-exposure NH_3 level to the plants. Similar results were obtained when *Calluna vulgaris* was exposed for 15 months to artificial rain containing different

levels of $(\text{NH}_4)_2\text{SO}_4$. In that experiment, the percentage of third instar larvae shed from the plants rose with increasing $(\text{NH}_4)_2\text{SO}_4$ concentrations (Van der Eerden et al., 1990a). Larval development and adult beetle weight were enhanced in plots fertilized with 400 kg ha⁻¹ NPK (56 kg N ha⁻¹) (Heil, 1984).

4.2.4 Pathogens

Several field observations indicate that trees are more susceptible to fungal infection under high nitrogen status (irrespective of the form and path of nitrogen enrichment, i.e. NH_y or NO_x , fertilizer application or atmospheric deposition) or altered nutrient balance such as increased N/K ratios (Ylimartimo, 1991). Roelofs et al. (1985) found that pine trees (*Pinus nigra* var. *maritima*) infected with *Brunchorstia pinea* or *Diplodia pinea* had higher needle N content than uninfected trees. The authors conclude that NH_y deposition from agricultural sources was responsible for elevated N content of the needles. In Belgium and The Netherlands, pine die-back near NH_3 sources was accompanied by infection with *Spheropsis sapinea*, most pronounced at close distances to intensive livestock operations or fields intensively sprayed with liquid manure (De Temmerman et al., 1987; Van Dijk et al., 1992).

Pinus sylvestris stands in Finland fertilized with NPK showed severe injury caused by infection with *Ascochyta abietina* (Vasander and Lindholm, 1985). The authors suggest nitrogen application caused late winter hardening, frost injury and subsequent weakening of the trees leading to fungal infection. Similar results were obtained in *Pinus radiata* (Australian pine) fertilized with 100 or 400 kg N ha⁻¹ yr⁻¹ resulting in increased arginine content and consequent infection with *Dothistroma* sp. correlating well with the arginine content (Lambert, 1986).

4.3 Mycorrhizae

Mycorrhizae are symbiotic associations between plant roots and fungi. Mycorrhizal associations are found virtually in every higher plant family (Harley, 1969). Those associations result in a number of benefits to the host plant: (1) longevity of the fine roots; (2) increased rate of nutrient absorption from the soil; (3) selective absorption of certain ions from the soil; (4) improved nutrient cycling; (5) resistance to certain root pathogens; (6) increased tolerance to soil toxins, cold temperatures, and high temperatures; and (7) tolerance to adverse soil pH and excess cations and anions (Hayman, 1978; Marx and Krupa, 1978). With the exception of the nutrient relationships and to a degree resistance to pathogens, mechanisms governing the other benefits are not well understood.

Symbiotic fungal infection of plant roots and successful mycorrhizal development depends on the supply of carbohydrates from the host to the fungus. In return, the fungus supplies the host with otherwise limiting nutrients, including N. There is evidence that plants adapted to N limiting soils (e.g., conifers, members of the cucumber family) have evolved with an N conservation mechanism, ornithine or urea cycle in their root system. While most amino acids contain one atom of N, intermediates in the ornithine cycle such as citrulline and arginine contain 2 and 3 N atoms per molecule. In the absence of mycorrhizal association, this cycle becomes non-operational due to mineral deficiency and more importantly, because the bi-product of the conversion of arginine to ornithine, urea, is toxic to higher plants. Mycorrhizal infection resulting in sufficient supply of minerals to the host roots removes the blockage of the ornithine

cycle leading to the availability of additional N and efficient amino acid metabolism and protein biosynthesis in the root. Equally importantly, most microorganisms including mycorrhizal fungi have the enzyme urease that detoxifies the urea released during the conversion of arginine to ornithine, the latter leading to the formation of glutamate, a key amino acid (Krupa et al., 1973; Krupa and Bränström, 1974) (also see section 3, b and Figure 2 in this chapter).

As discussed earlier, NH_y assimilation requires carbon skeletons and may thus compete with mycorrhizal sinks and inhibit mycorrhizal development and growth. Since mycorrhizae are of great importance for ion uptake, nutrient imbalances caused by NH_y uptake may further be increased (Bledsoe and Rygiewicz, 1986). It is well known that fertilization of forest stands can reduce mycorrhizal development (Menge and Grand, 1978). Therefore, it has been suggested that atmospheric nitrogen deposition has similar effects as fertilizer application (Nihlgård, 1985).

Reduction in mycorrhizae after NH_y exposure has been reported in several studies. Van der Eerden et al. (1992) found a distinct reduction of mycorrhizal infection in roots of *Pseudotsuga menziesii* exposed to NH_3 . Roots of *Calluna vulgaris* fertilized with 0, 40, 80 or 120 kg N ha⁻¹ exhibited significantly decreased mycorrhizal infection (Mickel et al., 1991). Field observations in pine forests near to huge pig farms showed a decline in mycorrhizal frequency in the upper soil horizon and a reduction of vital mycorrhizal cells (Hofmann and Heinsdorf, 1990). Heijne et al. (1992) tested the reaction of *Antennaria dioica*, *Arnica montana* and *Hieracium pilosella* (mouse-ear hawkweed) to $(\text{NH}_4)_2\text{SO}_4$ in greenhouse and field experiments. They found the percent vesicular-arbuscular mycorrhizal (VAM) infection to increase in *Antennaria dioica*, remain unchanged in *Hieracium pilosella* and decrease in *Arnica montana*, a species found to decline in Dutch heathlands, after two years of field exposure to $(\text{NH}_4)_2\text{SO}_4$.

5.0 INTERACTIVE OR JOINT EFFECTS OF NH₃ WITH OTHER AIR POLLUTANTS ON VEGETATION

Very few experiments have been conducted to study the combined effects of NH₃ with other air pollutants such as SO₂ or ozone (O₃). Since one of the effects of O₃ is to accelerate leaf senescence (Pell et al., 1997), and conversely since NH₃ is known to prolong the growth period and retard senescence (Fangmeier et al., 1994), one might expect O₃ and NH₃ to negate the effects of each other. However, the modes of action of these two pollutants are completely different. The toxic effects of O₃ *per se* are dependent on the amount of uptake and detoxification by the antioxidant defense system of the plants (Pell et al., 1997). Since the antioxidant systems require energy to operate, even successful detoxification of O₃ may increase the plant sensitivity to NH₃ by decreasing the amount of energy available for NH₃ assimilation. Another aspect to be considered is that NH₃ exposure tends to cause stomatal opening. Thus the amount of O₃ uptake may be increased in the presence of NH₃.

Van der Eerden et al. (1989) exposed Douglas fir saplings to NH₃ and O₃ and did not observe any visible injury, however, the pollutant combination caused erosion of the epicuticular wax layer. Both NH₃ and O₃ altered the plant nutrient (K, Mg and P) content. Van der Eerden et al. (1994) exposed an O₃-sensitive bean cultivar to a range of O₃ concentrations with and without the addition of NH₃. Leaf injury by O₃ was reduced in the presence of NH₃, while biomass production was stimulated by NH₃ and reduced by O₃ with no statistically relevant interaction.

Sulphur dioxide and NH₃ are deposited together, since the deposition of one compound is enhanced by the other (Adema et al., 1986; Van Hove et al., 1989b; McLeod et al., 1990; Bobbink et al., 1992a; Dueck and Elderson, 1992) and the two pollutants may be thus expected to act synergistically. Photosynthesis in *Populus euramericana* saplings exposed to NH₃ and SO₂, however, showed an antagonistic response; it was increased by NH₃, and that effect was cancelled by a combination with SO₂ (Van Hove et al., 1991).

Synergistic effects were found in several experiments with heathland species exposed to NH₃ and SO₂ in open-top chambers. Mortality of *Calluna vulgaris* seedlings after long-term fumigation with NH₃ and SO₂ increased synergistically (Dueck, 1990) and frost resistance of *Pinus sylvestris* decreased and needle injury was increased (Dueck et al., 1990). In this experiment, smoothening of epicuticular waxes of *Pinus sylvestris* needles was observed only when NH₃ and SO₂ were present together and not after exposure to either pollutant alone.

Dueck and Elderson (1992) exposed *Arnica montana* and *Viola canina*, as mono and mixed cultures with *Agrostis capillaris*, to 90 µg m⁻³ (34 ppb) SO₂ and 50 µg m⁻³ (72 ppb) NH₃, singly and in combination, and studied the effects of the fumigants on competitive ability and plant nutrient status. No interactions between the two pollutants were found on growth parameters with one exception; the root biomass of *Agrostis capillaris* was reduced in a less than additive manner. However, nutrient content (S, N, P, K, Ca, Mg) in some cases was affected in more than an additive manner by SO₂ and NH₃. The same holds true for example, for an increase of root N content in *Arnica montana* and *Agrostis capillaris* and shoot K⁺ content in *Viola canina*.

In summary, the amount of available information on the interactive effects of NH₃ and NH₃ must be considered as too small to draw any general conclusions.

6.0 EFFECTS OF N DEPOSITION AT THE ECOSYSTEM LEVEL

Anthropogenic N input affects its status and cycling in ecosystems both through the soil and plant canopy deposition, leading to eutrophication of coastal marine waters (Burkart and James, 1999), and to acidification of the soils (Fenn et al., 1998) (also Figure 5). Since natural terrestrial ecosystems are usually N deficient (most of the N pool originates from N_2 -fixation rather than from weathering and is present as organic N), excess N from deposition is readily taken up and accumulated until saturation occurs. According to Tamm (1991), ecosystems in the saturation phase are characterized by an amount of N supply meeting all their requirements, with simultaneous leaching of NO_3^- . It is clear that N deposition has steadily increased during roughly the past 100 years, so that most ecosystems are assumed to be in the accumulation or already in the saturation phase.

Ecological modification and successional change by means of N deposition will be most obvious in systems poor in N, because species adapted to N deficiency will soon be out-competed by species with higher N demand (Aerts, 1990; Tilman and Wedin, 1991). Therefore, species diversity may be severely reduced by nitrogen eutrophication (Ellenberg, 1985). Besides eutrophication, acidification may cause floristic alterations, as was shown in deciduous forests (Falkengren-Grerup, 1986, 1989) or in heathlands (Roelofs, 1986). Overall, nitrogen deposition may have severe consequences for species diversity and nature conservation (Woodin and Farmer, 1993). For example, many of the threatened species in central Europe are most abundant in semi-natural systems (e.g., species-rich grasslands, heathlands), the maintenance of which is dependent on management (aspects relevant to the removal of nutrients). Current management practices, however, do not provide any mechanisms to protect these systems from atmospheric deposition (Woodin and Farmer, 1993).

6.1 Soil Processes

Nitrogen saturation and acidification of the soil are symptoms of changes in a complex network of interacting processes that are influenced by atmospheric input and indirectly by effects on vegetation and soil microflora and microfauna. The population of soil microfauna generally declines due to acidification and as a consequence decomposition and mineralization of organic matter slows down (Van Straalen et al., 1988). Decomposition and mineralization of organic material is also influenced by N deposition via its impact on biomass production and the chemical composition of the vegetation (Berendse, 1990).

6.1.1 *N Saturation*

Unfertilized terrestrial ecosystems are usually characterized by relatively closed N cycling, i.e., N input and output are comparably small in relation to N exchange within the soil/plant subsystem (Fenn et al., 1998). In these ecosystems, N is usually limiting for productivity and additional nitrogen is readily absorbed and utilized. If deposition exceeds the capacity to utilize N for a considerable period of time, over-saturation of the system (Tamm, 1991) indicated by N loss (Nilsson et al., 1988; Tamm, 1989; Rosén et al., 1992) will occur. N loss may occur either by leaching of NO_3^- which is more mobile than NH_4^+ (Grennfelt and Hultberg, 1986) or by

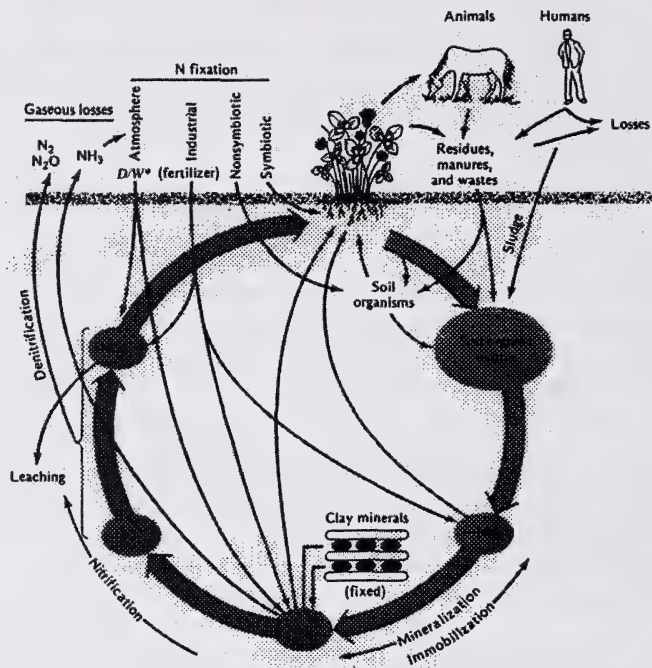


Figure 5 The nitrogen cycle, emphasizing the primary biological transformations (large shaded circle) the means of replenishment and the losses from the soil. Chemical fertilizers from industrial nitrogen fixation are an increasingly important source of this element, but excessive use has serious environmental implications. D/W = Respectively, dry and wet atmospheric deposition. Source: modified from Brady (1990)

denitrification, yielding N_2 and some N_2O . The latter gas is emitted at higher rates from soils polluted with NH_4^+ (Magalhaes et al., 1984; Tietema and Verstraten, 1991) and contributes to the greenhouse effect and the destruction of the stratospheric ozone layer (Houghton et al., 1990).

According to Fenn et al. (1998) there are several N saturated forests in North America Table 5). Among those is Turkey Lakes Watershed in Ontario. Nitrogen saturation is thought to progress through three stages as N inputs increase in the forest (Aber et al., 1989). Stage 0 is the typical condition of N limitation. Stage 1 occurs when N concentrations in the foliage and possibly in tree production increase and brief periods of N losses from the system are temporarily amplified. In stage 2, N losses from the forest are sustained and nitrification increases. In most cases, reports of N saturation pertain to stage 2. In stage 3, chronic N inputs lead to forest decline or decreased productivity. For a detailed discussion of N excess in the North American forest ecosystems, predisposing factors and the ecosystem responses, the reader should consult Fenn et al. (1998).

In Canada, the highest N deposition and NO_3^- concentrations in surface waters occur in southcentral Ontario and southwestern Quebec. The highest N deposition ($13 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) is moderate compared to the high deposition areas in Europe and the US (Jeffries, 1995). Lac Laflamme in Quebec and Turkey Lakes in Ontario exhibit NO_3^- export patterns of stages 1 and 2 respectively of watershed N saturation (as per Stoddard, 1994). Moderate NO_3^- export to lakes occurs in many watersheds in southeastern Canada. In regions with the lowest N deposition (Newfoundland and Labrador), NO_3^- concentrations in the lakes are near zero (Jeffries, 1995).

6.1.2 Acidification

NH_4^+ deposited to the soil may either be taken up by plant roots or be subjected to nitrification yielding NO_3^- (Figure 5). Since both processes result in proton release into the soil, acidification will occur, particularly in acid soils with low buffering capacity. Subsequently leaching of cations such as K^+ , Ca^{2+} and Mg^{2+} leading to nutrient imbalances for plant growth and release of toxic ions such as Al^{3+} may occur (Van Breemen et al., 1984; Reuss et al., 1987; Nilsson et al., 1988; Van Dijk et al., 1989; Tomlinson, 1991).

The acidifying potential of nitrogen may be calculated as $(NH_4^+ \text{ input} + NO_3^- \text{ output}) - (NH_4^+ \text{ output} + NO_3^- \text{ input})$ assuming a negligible change in storage of NH_4^+ and NO_3^- in the soil system. If this term yields values greater than zero, acidification is to be expected (Prinz, 1990).

6.2 Ecosystem Responses

6.2.1 Effects on Heathlands

The most obvious vegetation change in Dutch heathlands during the past decades has been their transition into grassland (Heil and Diemont, 1983), both in dry (dominated by *Calluna vulgaris*) and wet heathlands (dominated by *Erica tetralix*, cross-leaved heath). Similar vegetation changes were observed in northern Germany (Steubing and Buchwald, 1989).

These vegetation changes in heathlands have been intensively studied, and much evidence is available now from both field observations and exposures with model plant communities showing that transition of heathland into grassland is induced even at low levels of N deposition.

Calluna vulgaris or *Erica tetralix* may successfully compete with grasses even at high rates of N deposition as long as the canopies are closed, providing only insufficient solar radiation for new seedlings to emerge (Aerts et al., 1990). However, N deposition causes nutrient imbalances, increases the shoot/root ratio and, thus, increases the sensitivity of the dwarf-shrubs to drought stress, frost stress, and heather beetle attack (Heil and Diemont, 1983; Heil, 1984; Van der Eerden et al., 1991). These processes lead to gaps in the canopy, which then may be readily invaded by grasses that are more efficient in utilizing additional N, gaining a competitive advantage. Grasses replacing dwarf-shrubs have been shown to utilize NH_3 better than *Calluna vulgaris* (growth enhancement: *Molinia caerulea*, moor grass > *Deschampsia flexuosa* > *Calluna vulgaris* (Van der Eerden et al., 1990a). After NH_3 exposure, both shoot and root growth of *Deschampsia flexuosa* was increased, whereas *Calluna vulgaris* responded only with the shoot growth (Van der Eerden et al., 1991). Similarly allocation of NH_3 from the shoots into the roots was significantly greater in *Deschampsia flexuosa* than in *Calluna vulgaris* (Dueck et al., 1991). Long-term fumigations with NH_3 caused mortality in *Calluna vulgaris*, not observed in *Deschampsia flexuosa* and *Molinia caerulea* (Van der Eerden et al., 1991). In general, grasses appear to have higher nutrient-use efficiency than dwarf-shrubs, as was shown by Aerts (1990) who compared nutrient-use efficiency of *Erica tetralix*, *Calluna vulgaris* and *Molinia caerulea*.

Besides weakening the competitive abilities of dominating dwarf-shrubs, N deposition, in particular NH_y by its acidifying effects, was responsible for a decrease in species diversity in heathlands (Van Breemen and Van Dijk, 1988). Acidification from NH_y deposition may lead to the disappearance of species-rich microhabitats with higher pH, thus threatening species such as *Thymus serpyllum* (thyme) or *Pedicularis sylvatica* (lousewort) (Roelofs, 1986; Roelofs et al., 1987a). Acidification is also held responsible for the decline of *Arnica montana* (and other species of the *Viola canina* group) in Dutch heathlands, since it is well correlated with low soil pH, low levels of available base cations and high $\text{Al}^{3+}/\text{Ca}^{2+}$ ratios (Fennema, 1992).

Drastic alterations have been reported in cryptogamic (flowerless, seedless plants) vegetation of Dutch heathlands. Van Ree and De Smidt (1989) compared recordings of moss and lichen flora in the province of Gelderland from 1965 to 1975 with mappings in 1988 and found that 25 cryptogamic species have been nearly or completely lost. Average moss cover declined from 50-60% in 1965-1975 to 2-10% in 1988 within the heathland areas. This is attributed both to direct effects of eutrophication, as well as to an increase of dense grass canopies preventing moss growth. Drastic loss in species was observed in liverworts, with only 3 of the 13 species found in 1965-1975 still being present in 1988. In a similar manner, 12 of the 18 lichen species commonly found have disappeared or become rare.

6.2.2 Effects on Species-rich Grasslands

Associations of the Mesobromion (meadow) related species belong to the plant communities with the greatest species diversity known in central Europe. Many threatened species adapted to low nutrient availability are common in the Mesobromion group. The conservation of these calcareous grasslands demands regular management (mowing and removal of the hay) to keep the nutrient status at a low level.

In Dutch calcareous grasslands, an increase in dominance of *Brachypodium pinnatum* (false-brome) was observed during the past decade (Bobbink, 1991). The dominance of *Brachypodium*

pinnatum, however, is negatively correlated with species diversity in these systems (Bobbink and Willems, 1987). In fertilizer experiments with N, P or K and NPK, growth and competitive ability of *Brachypodium pinnatum* were significantly increased by N or NPK addition (Bobbink, 1991). The grass species benefited from N input more than other chalkland species without suffering from lowered P availability caused by N-induced growth stimulation. Thus, N deposition severely reduces species diversity in calcareous grasslands by promoting the dominance of *Brachypodium pinnatum*.

6.2.3 Effects on Forests

Until the 1980-1990s, the 'classical' forest decline theories such as due to SO₂ pollution or acidic rain were most popular. However, at the present time, it is well accepted that forest decline is a result of complex interactions of both of natural and anthropogenic stresses. These include climatic events, e.g., early or late frost, drought periods and biotic stress such as pathogens and pests, management practices, air pollution, and possibly global climate change (McLaughlin, 1985; Krause et al., 1986; Klein and Perkins, 1988; Innes and Oleksyn, 2000).

Nihlgård (1985) was the first to consider N deposition from NH_y and NO_x as significant contributors to forest decline in Europe. Taking into account all the direct and indirect effects of N deposition previously described and considering the receptor qualities of forest canopies to atmospheric deposition, N deposition must indeed be regarded as a factor severely disturbing nutrient cycling in forest ecosystems with detrimental effects for tree health.

While some of the N deposited on tree canopies is directly taken up, the rest accumulates on canopy surfaces, contributing to the throughfall deposition (Lindberg et al., 1986). Forest canopy N deposition by far exceeds bulk deposition above the canopy and deposition to forest edges again exceeds deposition into the closed forest (Grennfelt and Hasselrot, 1987). Even in areas like southern Sweden that are nearly exclusively polluted by long range transport, average N deposition to forests is approximately 20 kg ha⁻¹ yr⁻¹, with extreme values greater than 40 kg ha⁻¹ yr⁻¹ (Grennfelt and Hultberg, 1986). At these amounts of deposition, NO₃⁻ leaching from the system has already been observed, indicating that N saturation has taken place.

The decline of Norway spruce forests in northern Bavaria (Fichtelgebirge) subjected to different types of pollutants has been mainly attributed to nutrient imbalances (Schulze, 1989). In that geographic area, gaseous pollutants such as SO₂, NO₂, and O₃, in spite of being present at rather high concentrations, had no long-lasting direct effects on needle physiology (e.g., gas exchange). Soil chemistry and plant nutrition, however, were significantly altered by deposition of SO₄²⁺, NO₃⁻, and NH₄⁺ causing N/cation imbalance in the tissue, with severe secondary effects.

Areas highly polluted with N are found in The Netherlands, Belgium (De Temmerman et al., 1987), and areas of northern Germany and at least by 1990 in East Germany when many intensively managed livestock operations were shut down. N deposition in the forests in Netherlands is typically around 80 kg N ha⁻¹ yr⁻¹ (Houdijk and Roelofs, 1991) and deposition of 115 kg ha⁻¹ yr⁻¹ was found in Douglas fir stands at a distance of 30 km from intensively managed agricultural areas, 83% resulting from NH_y deposition and 17% from NO_x deposition (Draaijers et al., 1989; Ivens et al., 1989). Acidification leading to the leaching of NO₃⁻ and cations and release of Al³⁺ occurs in the acidic soils that are mainly impoverished in nutrients and low in

their buffering capacity (Van Breemen et al., 1982; Van Breemen and Van Dijk, 1988), thus severely reducing the vitality of the trees.

Detailed investigations on the decline of pine forests around intensively managed livestock operations have been carried out near Eberswalde (former East Germany), where a farm with up to 20,000 pigs was in operation until 1991 (Hofmann and Heinsdorf, 1990; Hofmann et al., 1990; Heinsdorf and Krauß, 1991). Canopy N deposition in these Scotch pine forests was up to 150 kg ha⁻¹ yr⁻¹. The forests showed distinct zonation with particular injury symptoms dependent on the distance from the source. At greater distances, N accumulation resulted in increased tree growth, followed by areas with N saturation as indicated by the N content of the needles above 1.8%. Closer to the source, further increase of N deposition resulted in soil acidification, leaching of cations, fine root destruction, reduction in mycorrhizae and development of visible needle injury, further enhanced by direct effects of NH₃ present at toxic levels. At distances less than approximately 1 km from the source, the forests were completely destroyed. Dwarf shrubs such as *Calluna vulgaris* and *Vaccinium vitis-idaea* normally occurring in these forests disappeared and the grasses *Calamagrostis epigeios* (reedgrass) (at sites naturally somewhat more enriched with nutrients) or *Deschampsia flexuosa* (at poor sites) dramatically increased in their coverage. Since the grass layer may compete with pine for water supply, further susceptibility to drought stress, in particular because of the dry climate in this region, occurred as an indirect effect of N deposition. Besides changes in the herb layer, invasion of shrubs such as *Prunus serotina* (black cherry) and *Sambucus nigra* is visibly promoted in these pine stands.

Overall tree vitality is likely a relatively insensitive indicator for N saturation effects on the forest ecosystem. More sensitive indicators are species composition of the herbaceous (Steubing and Fangmeier, 1991) and epiphytic vegetation, including bryophytes, lichens and the mycorrhizal fungi.

7.0 EFFECTS OF N DEPOSITION ON EPIPHYTIC LICHENS AND GREEN ALGAE

7.1 Lichens

Since the publication of Nylander (1866), epiphytic or tree bark inhabiting lichens (seedless, flowerless lower plants, products of symbiosis between algae and fungi) have been used in air pollution mapping studies (Haugsjå, 1930; Henderson, 1995a,b, 1996a,b, 1997a,b, 1998). Hawksworth and Rose (1970) developed a scale for estimating SO₂ concentrations from the observed lichen species.

Different epiphytic lichen assemblages are found on tree barks that are acidic or nutrient-poor (e.g., oak and beech) and neutral or nutrient-rich or “eutrophicated” (e.g., willow, elm and poplar) (Van Dobben and Ter Braak, 1998). Lichens in the first category are defined as “acidophytic”, while those in the second category are defined as “nitrophytic” (Brand et al., 1988; Wirth, 1991). The scale of Hawksworth and Rose (1970) also distinguishes between “acidic” and “eutrophicated” bark.

Van Dobben and Ter Braak (1999) studied the relationships between measured concentrations of SO₂, NO₂ and NH₃ and lichen abundance in the Netherlands (Table 6). They compared the observed relationships to published indicator scales of lichen sensitivity to air pollution. For SO₂, a good agreement was found between all the indicator scales and calculated sensitivities based on the presence or absence of a given species. For NO₂ and NH₃ the correspondence was less obvious. The sensitivity to NH₃ was inversely related to the Wirth’s (1991) acidity indicator scale. Species that react positively to NH₃, tended to be sensitive to SO₂ and NO₂.

Although at the outset, increases in the abundance of “nitrophytic” lichens may appear to be correlated with increases in N deposition, such lichen species appear to have become more common with decreases in SO₂ concentrations and/or S deposition (acidification) (Poikolainen et al., 1998a; Van Dobben and Ter Braak, 1998).

Van Dobben and Ter Braak (1998) proposed three hypothetical mechanisms to explain the strong increase in the “nitrophytic” lichens in responses to decreasing SO₂ concentrations:

- Decreasing SO₂ concentrations may have resulted in an upward trend in bark pH. “Nitrophytic” lichens prefer high bark pH.
- “Nitrophytic” lichen species appear to be more sensitive to SO₂ than others.
- “Nitrophytic” lichen species respond more rapidly than others to sudden decreases in SO₂ concentrations. This suggests that under ameliorating conditions, “nitrophytic” species can colonize new sites more rapidly than others.

There are fundamental differences in the effects of atmospheric SO₂ and NH₃ on terrestrial higher plants and epiphytic lichens (Table 7). Nevertheless, in environmental research, conclusions are frequently based on univariate studies. But, under ambient real world conditions, it is difficult to separate the influence of many interacting variables. Although

lichens can be used as excellent indicators of environmental stress, the value of epiphytic lichens as accumulators of air pollutants, have not been exploited by biological effects scientists in studies of source apportionment (Sloof, 1995). Until such studies are fully expanded, it would be difficult to establish more definitive cause-effect relationships.

7.2 Green Algae

As noted previously in this report, N deposition has a two fold ecological impact. 1. N causes acidification of the soil due to leaching of base cations and 2. It is a vital plant nutrient, which in excess causes eutrophication. It has been observed that increased N deposition resulted in changes in vegetation, especially in areas of high deposition in Central Europe, to the extent eutrophic plant species have increased at the expense of oligotrophic species (Bobbink et al., 1992c; Sutton et al., 1993). At the same time, epiphytic algae have increased especially on Norway spruce (*Picea abies*) needles in the southern parts of Fenno-scandia and in Central Europe (Göransson, 1988, 1990; Bråkenhielm and Liu Qinghong, 1995).

Poikolainen et al. (1998b) reported an increased abundance of epiphytic green algae on conifers in Finland during 1985-1995. Abundance of green algae was the highest in southern Finland where N deposition is highest. According to the authors, the abundance of green algae may have been caused by several concurrent changes in the environment. A slight increase in mean annual temperature, a long-term stability in N deposition and a clear decrease in S deposition may all have contributed to the increased growth and abundance of green algae. At a local scale, variations in the microclimate due to nutrient richness of the habitat, the predominant tree species, stand age and density, all have an effect. As in the case of lichens, multi-variate, source apportionment studies are required to better explain the relationships between N deposition and the distributions of epiphytic green algae.

8.0 AIR QUALITY INDICATORS FOR PROTECTING VEGETATION

The critical level/critical load concept has been followed in many countries since over some two decades and has been widely accepted as an appropriate tool to provide estimates of target levels/target loads for decision makers (Bull, 1991).

8.1 Critical Levels

Critical levels are defined as 'the concentrations of pollutants in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials may occur according to present knowledge' (UNECE, 1988).

8.2 Critical Loads

Critical loads concept was originally developed in Canada in the 1970s. Critical loads are defined as 'A quantitative estimate of an exposure to one or more pollutants below which harmful effects on specified sensitive elements of the environment do not occur according to present knowledge' (Nilsson and Grennfelt, 1988).

There is inevitably some debate on how to define 'adverse or harmful effects'. In particular, this is true for NH_3 that acts as a fertilizer at low concentrations without any detectable (primary) toxic effects. However, secondary effects such as increased susceptibility to stress or altered competitive ability (mostly not investigated or not detected in short term experiments) may occur. Nevertheless, the United Nations Economic Commission for Europe (UNECE, 1994) has adopted the critical loads approach.

8.2.1 Critical Levels (NH_3)

Table 8 provides a listing of critical levels for NH_3 given by different investigators. The values obtained by Van der Eerden (1982) and Posthumus in UNECE (1988) were estimated using the 'envelope' method, i.e., by a graphical approach plotting all data from NH_3 exposures causing adverse effects in a concentration/time frame and fitting a curve directly below the lowest effective exposure levels. According to Fangmeier et al. (1994), that approach, however, may not be appropriate for several reasons. First, one has to take into account that the data used, originated from very diverse experimental approaches. The sensitivity of plants to air pollutants significantly differs depending on the (climatic and experimental) exposure conditions. Plants grown under constant growth conditions in controlled environment chambers or in greenhouses usually differ in their sensitivity from plants grown outside and hardened by diurnal climatic variation. Secondly, since experimental designs usually include the exposure of plants to certain concentrations for certain periods of time, the true lowest concentration or duration of exposure causing adverse effects will not be correctly determined, since the entire response surface is not being defined. Using eco-toxicological models that include repair and compensation factors may yield more appropriate results. Van der Eerden et al. (1991) used a toxicological model described for water pollution by Kooijman (1987) and for soil pollution by Van Straalen and Denneman (1989) to recalculate critical levels for NH_3 . Those values are shown in Table 8 and are far below the previous estimates.

Fangmeier et al. (1994) tried to apply the ecotoxicological model to estimate critical levels for four different groups of plants: (a) natural vegetation as a whole, (b) most sensitive species such as members of the *Viola canina* group and mosses, (c) trees and (d) agricultural crops (Hadwiger-Fangmeier et al., 1992). However, the amount of available data (observations) was too small in many cases, to calculate critical levels for NH_3 for corresponding plant groups. Nevertheless, the range of susceptibility to NH_3 was suggested to be: natural vegetation > forests > crops, assuming forests to include managed systems and natural vegetation to include native woodlands.

More recently, Van der Eerden et al. (1998) provided an estimate of the risk of NH_3 damage to sensitive crops in relation to the distance to the source, based on the mean and variations in the emissions, plume dispersion, regional background concentration, landscape characteristics and plant sensitivity. The results of the application of the model NOEL (No Observable Effect Levels) are presented in Figure 6. The reliability of the method was determined by the quality of the information or data used and the authors state that several possibilities for over- or under estimations exist and discuss various precautions that should be taken in applying their model.

8.2.2 Critical Loads (N)

Examples of estimates and model calculations of critical loads of N are presented in Table 9. In many cases (particularly in Europe), current N deposition by far exceeds those critical load values. In a 1996 report by the Danish Environmental Protection Agency (full English translation not available, see <http://www2.mst.dk/magazile/issue1/ammonia2/fakta1.htm>), critical loads stipulated for ammonia and other N species was 5 and 10 $\text{kg ha}^{-1} \text{yr}^{-1}$ for heaths and bogs respectively. For forests, 10-20 $\text{kg ha}^{-1} \text{yr}^{-1}$, depending on the soil conditions. According to the report, if N deposition were evenly distributed across entire Denmark, it would equal an average of 21 $\text{kg ha}^{-1} \text{yr}^{-1}$, with 14 kg attributable to NH_3 and the remaining 7 kg to NO_x (primarily fossil fuel combustion).

Natural and semi-natural ecosystems, as well as forests must be expected to be severely at risk from the current amount of N deposition. Agricultural crops appear to be the only systems not negatively influenced at present, since high productivity and turnover prevent the accumulation of N. In the overall analysis, one should keep in mind, however, that N_2O release to the atmosphere and NO_3^- leaching into the ground water by agricultural systems represent serious problems, which may be increased by N deposition into these systems.

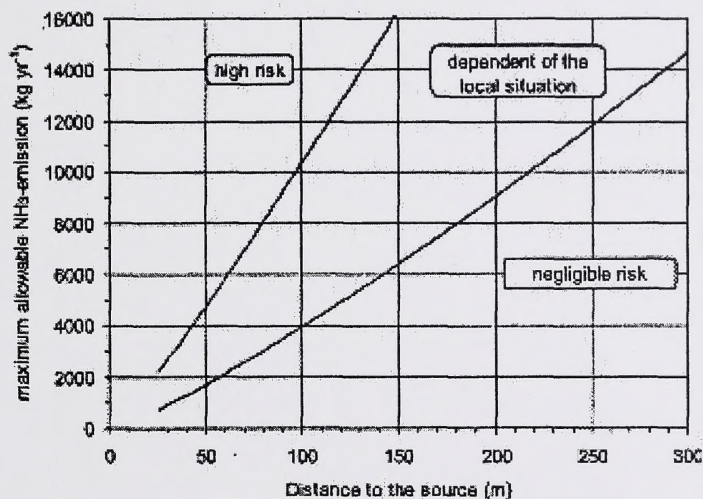


Figure 6 Modeled relationships between the maximum NH_3 emissions, with no exceedances of the 'no observable effect level' and distance between the source and a sensitive receptor. Area above the upper curve indicates that the emissions are too high or the source is at a too short a distance from the sensitive receptor. The lower curve indicates situations where the prevailing wind direction is from the source to the sensitive receptor. While the lower curve reflects high background NH_3 concentrations, the upper curve reflects the opposite. Source: Van der Eerden et al. (1998)

